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Performance of Chromium Exchanged Zeolite Catalysts in the Combustion of Volatile Organic Compound Pollutants

Ahmad Zuhairi Abdullah
Mohamad Zailani Abu Bakar
Subhash Bhatia
Fax: +604-594 1013
Email: chbhatia@eng.usm.my
School of Chemical Engineering,
Universiti Sains Malaysia, Engineering Campus,
Seri Ampangan, Nibong Tebal, 14300, Penang, Malaysia.

The activity and stability of chromium exchanged beta (Cr-BEA), mordenite (Cr-MOR) and ZSM-5 (Cr-ZSM-5) zeolites of different Si/Al ratios for volatile organic compounds (VOCs) combustion are reported. A fixed-bed catalytic reactor operated between 100° and 500°C and at a GHSV of 32,000 h^{-1} was used for activity study. Methanol, ethyl acetate, methyl ethyl ketone, benzene, hexane, toluene and xylene, all at 2,000 ppm, were selected as VOC model compounds. Oxygenated VOCs were more reactive while showing good carbon dioxide yield. Aromatics were more stable due to resonance effect but the reactivity increased with the attachment of electron donor groups such as methyl group. Cr-ZSM-5(240) demonstrated the highest hydrothermal stability due to its high Si/Al ratio. Despite giving the high initial activity due to high metal loading, Cr-BEA(25) was susceptible to coking in the long run. The high coke formation in mordenite and beta zeolites was associated with their high acidity, the presence of interconnecting channels of different sizes and the relatively larger pore sizes. Coke forming on Cr-ZSM-5(240) was more carbonaceous and oxidized at higher temperatures.

Keywords: VOC, combustion, zeolites, stability, deactivation and coke.

INTRODUCTION

Volatile organic compounds (VOCs) are emitted in dilute concentrations from many industrial processes and catalytic combustion is considered to be an effective way for the abatement of these emissions. This process is similar to thermal combustion in that the gaseous organic impurities to be destroyed are reacted with oxygen at elevated temperatures to form primarily carbon dioxide and water (Zhang et al., 1997). It differs from thermal combustion because in catalytic combustion, the reaction occurs at relatively lower temperatures (150° to 480°C) by the use of solid catalysts (Kohl and Nielsen, 1997). This lower operating temperature translates as lower

energy requirement to run the catalytic unit.

The reactivity of VOCs to be catalytically decomposed is influenced by their chemical nature (Isaacs, 1995). A model VOC for combustion study is generally selected on 'worst player' basis that is the most difficult compounds to be decomposed. However, there are cases where the reactivity of a VOC is catalyst specific. Ordóñez et al. (2002) found that benzene was more reactive than toluene over Pt/Al_2O_3 while Petterson et al. (1999) reported higher reactivity of toluene over Rh/Al_2O_3.

Beside conventional catalyst supports being used for VOC catalytic combustion such as alumina, silica and titania, zeolites are among the potential supports that are actively being investigated for their role in this process (Becker and Förster ; Niu et al., 1999). Some promising results have been reported using zeolite Y (Karmakar and Greene, 1992 ; Dégé et al., 2000) and ZSM-5 (Chintawar and Greene, 1997) to host active metal species. The stability of ZSM-5 is reported to be much higher compared to that of zeolite Y for high temperature and also more suitable for application under high humidity (Chintawar and Greene, 1997 ; Atwood et al., 1998). Limited information is available on other zeolites such as beta (BEA) and mordenite (MOR) despite having found application in many industrial processes. These zeolites possess higher surface area and organic sorption than ZSM-5 (Chen et al., 1994). Together with their characteristic pore structures, difference in the behaviour of their supported catalysts in VOC combustion application is expected.

Catalyst coking in zeolite catalyzed reaction is a function of acidity and pore structure (Blauwhoff et al., 1999). Coke formation results from undesirable side reactions occurring on strong acid sites that are responsible for hydrogen transfer reactions (Sahoo et al., 2001). Pore structure plays significant role in coke accumulation process as it affects the condensation of coke and/or coke precursors which normally made up of polyaromatic rings (Antunes et al., 2001). Generally, zeolites with narrow pore mouth (windows) while having sinusoidal channel system are more susceptible to coking (Chen et al., 1994). In most reactions, three dimensional interconnected pores system will minimize coke accumulation as it allows the exit of coke precursors from any of its pore mouth (Blauwhoff et al., 1999). In this type of pore system, the tendency of coke accumulation on the channel intersections are reported by several authors (GUisnet et al., 1999 ; Bartholomew, 2001).

This paper addresses the reactivity study of various VOC model compounds and the combustion behaviour of the most stable organic compound. Comparative study on the hydrothermal stability and activity of chromium exchanged beta (Cr-BEA), mordenite (Cr-MOR) and ZSM-5 (Cr-ZSM-5) zeolites of different Si/Al ratios are also conducted. The amount and characteristics of coke accumulated on these catalysts are correlated with their acidity and types of pore system. Chromium has been used as active metal species in this study as it has been identified as the most active metal among the transition metals for VOC combustion (Zuhairi et al., 2003a ; Zuhairi et al.,

2003b).

EXPERIMENTAL

Zeolite beta (BEA, Si/Al=25 and 50), mordenite (MOR, Si/Al=40 and 90) and ZSM-5 (ZSM-5, Si/Al=90 and 240) were obtained from Süd-Chemie in their sodium form and were used as received. Chromium exchanged zeolites were prepared in two steps. In the first step, NH_4^+ exchange of the zeolite was performed in 2.25 M of NH_4Cl solution for 6 h. The metal exchange step was carried out in acidified (pH 4) 28.85 mmol/l of aqueous $Cr(NO_3)_3$ solution for 6 h, followed by filtration, drying and calcination at 550°C for 6 h. The chromium exchanged zeolites were pressed, crushed and sieved between 250 to 300 μm before used for activity studies. All zeolite samples were characterized for surface area using a Quantachrome Autosorb-1, final metal loading using a Shimadzu AA-6650 atomic absorption spectroscopy (AAS) and acidity via thermal desorption of ammonia (NH_3-TPD) using a Quantachrome Chembet 3000 system.

The catalytic activity test was performed in an 11 mm i.d. glass reactor charged with 0.2 gram of zeolite catalysts (Figure 1). The accurate control of the flow rates was achieved by means of Aalborg (AFC 2600) mass flow controllers. A VOC-laden stream was obtained by bubbling N_2 gas through a VOC saturator containing the required organic and another air flow was used to make up the total flow rate. The total flow rate was fixed at 250 ml/min to give corresponding GHSV of 32,000 h^{-1} while the concentration of organics in the reactor feed stream was fixed at 2,000 ppm. The inlet and outlet gases were analyzed using an off-line Shimadzu GC-8A gas chromatograph equipped with Porapak-Q and Molecular Sieve 5A columns for the separation of gas components. The components were detected by means of a thermal conductivity detector (TCD). Methanol (MeOH), ethyl acetate (EAc), methyl ethyl ketone (MEK), benzene (Bz), hexane (Hex), toluene (Tol) and xylene mixed isomers (Xyl) were taken as VOC model compounds.

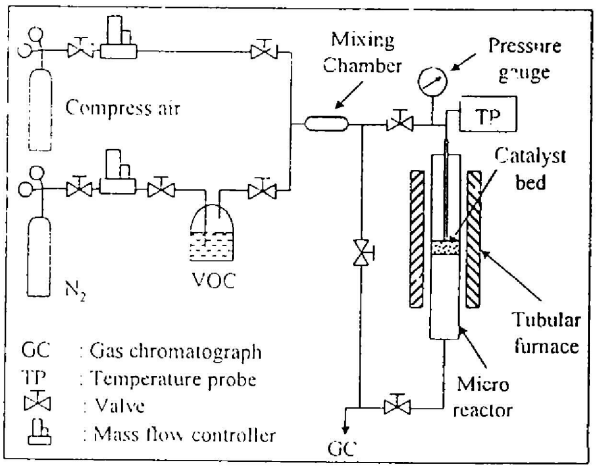

Figure 1. Experimental Set up for Catalyst Activity Measurement.

In the hydrothermal stability study, the catalyst samples were subjected to steam treatment at 500°C for 6 h. These hydrothermally treated samples were then characterized for changes in surface characteristics. The deactivation behaviour of the catalysts with time on stream was demonstrated by operating the catalytic reactor at a GHSV of 3,800 h^{-1} and at a reaction temperature of 400°C for up to 48 h. The conversion of ethyl acetate at a feed concentration of 25,600 ppm and corresponding carbon dioxide yield were taken to represent the catalytic activity. At the end of 48 h, the aged zeolite catalysts were taken out and characterized for surface characteristics to determine the extent of deactivation occurred. Thermal gravimetric analyses (TGA) in 20 ml/min of oxygen and at a temperature ramping rate of 10°C/min were also conducted to characterize the extent of coking and to study the oxidizability of the coke. The molar H/C ratios of the coke formed on the catalysts were determined using a Perkin Elmer elemental analyzer.

RESULTS AND DISCUSSION

Catalysts Characteristics

Table 1 summarizes the characteristics of zeolite catalysts prepared and used in the present study. In general, the BET surface area for beta was the highest followed by mordenite and ZSM-5. Chromium exchange procedure was found to cause less than 10 % drop in BET surface area. Corresponding reduction in micropore area was also detected while mesopore area was adversely affected. This could be due to the introduction of bigger Cr^{3+} cation in place of smaller Na^{+} cation into zeolites structure and partial structural changes due to heat treatment during chromium exchange process. The extent of chromium exchange was found to decrease as the Si/Al ratio of the zeolite increased attributed to lower capacity of framework charge compensation in higher Si/Al zeolites.

Lower Si/Al zeolites possessed higher acidity as aluminum atoms were associated with acid sites which could be in the form of Brønsted or Lewis acid sites. However, the relation was not straight forward to be generalized to different types of zeolite as the acidity was also determined by atomic arrangement in the framework structure and extra framework species present (13). It was noted in this study that Cr-ZSM-5(90) was less acidic compared to Cr-MOR(90) which had the same Si/Al value. Similarly, Cr-BEA(50) showed almost similar acidity compared to Cr-MOR(90) despite having much less aluminum content in its framework.

VOC reactivity study

Catalytic combustion of several selected VOCs measured based on the conversion and carbon dioxide yield are as depicted in Figures 2 (a) and Figure 2 (b), respectively. The conversion, and hence, the reactivity of oxygenated compounds such as methanol, ethyl acetate and methyl ethyl ketone was relatively higher compared to that of linear paraffin like *n*-hexane. On the other hand, aromatic compounds showed some degree of stability. The attachment of methyl group to benzene ring; one in

Table 1. Characteristic of Cr-exchanged Zeolites Samples as Compared to Their Original Na-form.

Catalyst[a]	S_{BET} (m^2/g)	Chromium Loading (%)	Pore Area		Acidity mmol NH_3/g
			Micro (m^2/g)	Meso (m^2/g)	
Na-BEA(25)	500	-	365	135	nd
Na-BEA(50)	557	-	430	127	nd
Na-MOR(40)	429	-	364	65	nd
Na-MOR(90)	413	-	319	94	nd
Na-ZSM-5(90)	374	-	291	83	nd
Na-ZSM-5(240)	393	-	321	72	nd
Cr-BEA(25)	488	0.99	341	147	0.83
Cr-BEA(50)	415	0.74	334	111	0.58
Cr-MOR(40)	419	0.88	359	70	0.78
Cr-MOR(90)	374	0.72	283	91	0.56
Cr-ZSM-5(90)	364	0.78	278	86	0.43
Cr-ZSM-5(240)	353	0.66	282	71	0.18

[a]Values in bracket denote Si/Al ratio of the zeolites.
nd=not determined

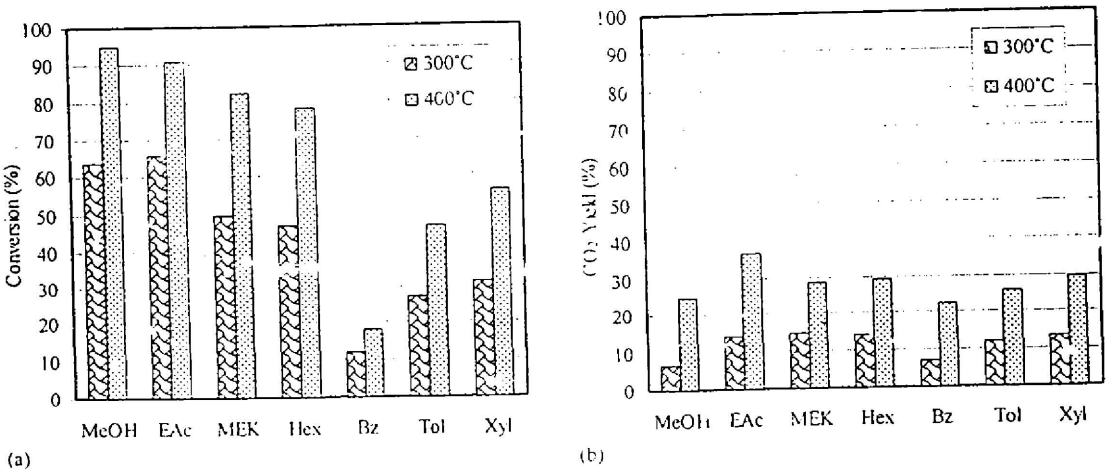

Figure 2. Conversion (a) and carbon dioxide yield (b) in the conversion of different organics at 300°C and 400°C. (Cr-BEA(25), GHSV=32,000 h^{-1}, C_{voc}=2,000 ppm).

toluene and two in xylene, was found to markedly improve the reactivity of these compounds.

Methanol, ethyl acetate and methyl ethyl ketone were more reactive as they had oxygen-containing groups which were well known electron-withdrawing groups, making the adjacent C-O and C-H bonds more susceptible to breakage. The oxygen atom also had unpaired electrons that can easily interact with vacant *p*-orbital of chromium ion in zeolite to form active intermediates. However, there was also stabilization effect that was brought about by the attachment of alkyl groups which were electron-donating groups. The stabilization of

methanol was attributed to the presence of a methyl group while in ethyl acetate, ethyl and methyl groups presented some stabilization effects on the carboxyl group. In methyl ethyl ketone, electron deficiency experienced by the carbonyl carbon atom was lessened by the attachment of methyl and ethyl groups. Consequently, this compound became relatively more stable compared to ethyl acetate and methanol.

Benzene was the least reactive substance due to the occurrence of resonance effect in its ring. Consequently, higher energy was required to cause the extraction of protons which would initiate its combustion. In toluene, methyl group did not possess a *p*- or π-orbital to conjugate with the π-molecular orbital of the aromatic system. Thus, the resonance effects were only limited to within the benzene ring. Since methyl was an electron-donating group, the stability of the substance was lowered as benzene ring itself was an electron-rich group. The effect manifested as marked increase in the conversion (reactivity) from benzene to toluene. In a similar way, the reactivity of xylene with two methyl groups was higher than that of toluene and benzene. The stability of these substances could also be seen from their ionization potential i.e. 9.24 eV (benzene), 8.82 eV (toluene), 8.56 eV (*o*-xylene) and 8.45 eV (*p*-xylene).

Despite readily decomposed, methanol, ethyl acetate and methyl ethyl ketone did not produce high carbon dioxide yield as suggested by Figure 2 (b). This was due to the occurrence of significant amounts of products of incomplete combustion in the outlet stream with these organics. Generally, they presented in the form of aldehydes and carboxylic acids. However, as in the reactivity, the carbon dioxide yield increased from benzene to xylene. With these aromatic compounds, the only product of incomplete combustion detected in the outlet stream was carbon monoxide.

Effect of zeolite supports on catalytic activity

Catalytic combustion of benzene as the most stable compound used in the present study was selected to be used for demonstration of the activity of various chromium exchanged zeolites. As shown in Figure 3, Cr-BEA(25) was the most active catalyst followed by Cr-ZSM-5(240). Cr-MOR at both Si/Al ratios was relatively less active with conversions of lower than 30 % in the temperature range studied. In terms of carbon dioxide yield, Cr-BEA(50) and Cr-ZSM-5(240) produced high and almost similar yield while those of mordenite supported catalysts did not even reach 50 % below 500°C. As a general trend, higher chromium loading in lower Si/Al BEA, MOR and ZSM-5 often resulted in higher conversion but at the expense of carbon dioxide yield.

Cr-BEA(25) was the most active catalyst used in the present study. With comparatively larger pore system and low Si/Al ratio, the exchange of chromium ion was favoured and consequently resulted in high chromium loading. An increase in Si/Al ratio from 25 to 50 weakened the chromium intake by the zeolite and the activity dropped accordingly as shown in Figure 3(a). Cr-ZSM-5 at both Si/Al ratios were moderately active as they possessed relatively lower surface area but uniform sized

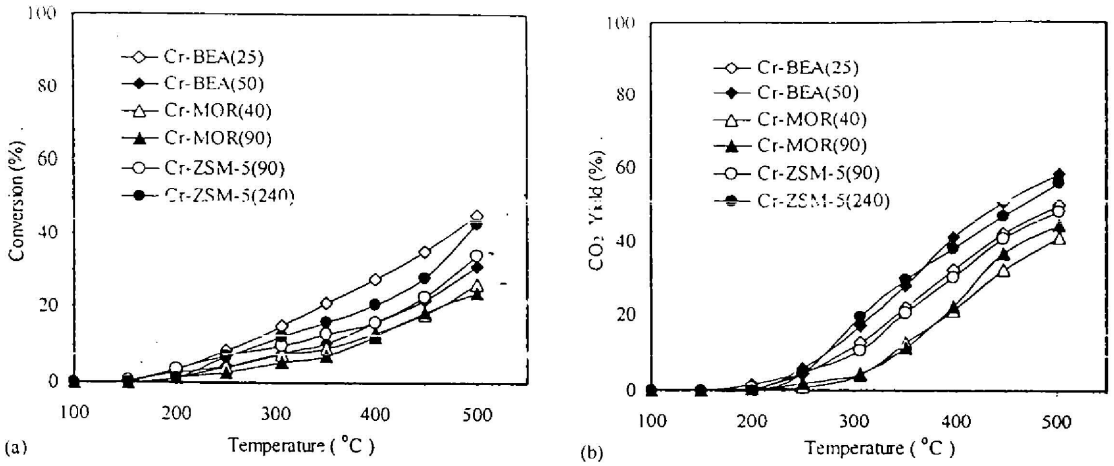

Figure 3. Conversion (a) and carbon dioxide yield (b) in the conversion of benzene (Bz) for different chromium exchanged zeolites. (GHSV=32,000 h^{-1}, C_{Bz}=2,000 ppm).

interconnecting channel system to allow easy diffusion of reactant and product molecules. Despite having higher chromium loading, Cr-ZSM-5(90) was less active compared to Cr-ZSM-5(240). This could be due to its higher hydrophobicity which generally increased with an increase in Si/Al ratio (Chintawar and Greene, 1997). Higher hydrophobicity translated as better organic sorption on this catalyst.

The low activities of Cr-MOR(40) and Cr-MOR(90) were partly attributed to their pore system. It should be noted that mordenite pore structure consisted of 12-membered ring channels that were crossed by 8-membered ring channels with aperture size of 2.8 x 5.7 Å. These apertures were actually windows rather than channels and were not readily accessible for benzene molecules due to steric effect (Chen et al., 1994). Therefore, the reaction was only limited at the external surface of the zeolite crystal. Shorter diffusion path of the reactant and/or intermediates also constrained the repeated oxidation of these substances to ultimately produce carbon dioxide. As a consequence, these two catalysts produced low carbon dioxide yield as noted in Figure 3 (b).

Hydrothermal stability test

Table 2 summarizes several changes in surface characteristics as a result of hydrothermal stability test. The treatment was found to eliminate some of the micropore while new mesopores were created. The reduction in micropore area varied from more than 70 % for Cr-MOR(90) to less than 10 % for Cr-ZSM-5(240) reflecting the stability of the letter. All three types of zeolites demonstrated higher stability with higher Si/Al ratio of the framework. In general, the most stable zeolite was ZSM-5 followed by BEA and MOR.

Changes in the surface characteristics of the catalyst upon hydrothermal treatment were attributed to the hydrolysis of Si–O–Si and Si–O–Al bonds in the framework of the zeolite support (Kühl, 1999).

Table 2. Effect of Hydrothermal Treatment on Surface Characteristics.

Catalyst	Percent Effect on*		
	S_{BET}	Micropore Area	Mesopore Area
Cr-BEA(25)	-16.4	-14.0	+31.5
Cr-BEA(50)	-9.6	-11.7	+17.2
Cr-MOR(40)	-51.3	-70.7	+41.0
Cr-MOR(90)	-21.7	-31.4	+8.6
Cr-ZSM-5(90)	-11.3	-17.0	+1.6
Cr-ZSM-5(240)	-6.2	-8.0	+1.2

*Relative to fresh catalyst

Owing to higher affinity of Si atom towards electron, O–Al bonds were relatively amenable to hydrolytic cleavage than O–Si to subsequently result in partial framework collapse. The effect manifested itself as a decrease in micropore area but with an increase in mesopore area. Therefore, higher hydrothermal stability demonstrated by higher Si/Al ratio zeolites was associated with less aluminum atoms in their framework. In addition, higher Si/Al ratio also translated as higher hydrophobicity of the catalyst to resist hydrolytic effect by water molecules at high temperature.

Effect of coking on activity

In the study of coking process, ethyl acetate was used as the test substance as it was found to cause the most serious coke accumulation compared to other substances. Profiles of conversion and corresponding carbon dioxide yield during ethyl acetate combustion with time on stream are as shown in Figure 4 (a) and Figure 4 (b), respectively. Cr-ZSM-5(240) showed the most stable conversion with only about 5 % drop in the conversion after 48 h time on stream. Despite quite stable for the first 18 h, Cr-BEA(25) experienced relatively sharper deactivation after this period. With Cr-MOR at both Si/Al ratios, sharper drop in the conversion was observed during the first 6 h after which, relatively stable activity was achieved. There was no clear trend observed for carbon dioxide yield except Cr-BEA(25) produced the best yield in the long run while the lowest yield was demonstrated by Cr-MOR(40).

The much lower coke production, and thus, much lower rate of deactivation of ZSM-5 catalysts were attributed to its three dimensional channel structure. The uniform channels and the absence of bottlenecks in its pore system easily permitted the entrance of feed molecules as well as the leaving of the product molecules (Chen et al., 1994). Other contributing factors were their low acidity and the geometrical constrain imposed by the 10-membered oxygen ring sized pores. The former factor translated as lower coke formation activity (Dégé et al., 2000) while latter factor made it sterically difficult to form large polynuclear hydrocarbons responsible for coking and irreversible deactivation (Chen et al., 1994).

Mordenite as well as beta exhibited high tendencies to coking as they were of higher acidity and possessed intersecting channels of two different sizes. Due to high acidity, the acid catalyzed dehydrogenation reaction was more active leading to fast coke formation, especially during early hours on stream. The effect was more noticeable in smaller pore sized mordenite compared to bigger pore sized beta zeolite. The channel intersection generally acted as a window to trap coke precursors and

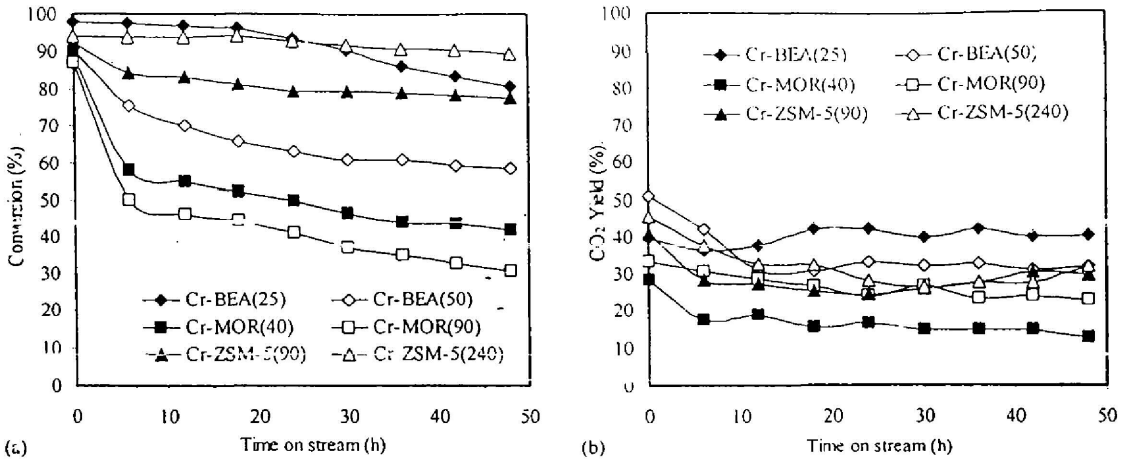

Figure 4. Profile of ethyl acetate (EAc) conversion (a) and carbon dioxide selectivity (b) with time on stream. (Reaction temperature=400°C, GHSV=3,800 h^{-1}, C_{EAc} =25,600 ppm).

and up as coke deposit in the large 12-membered oxygen ring openings (Chen et al., 1994 ; Bartholomew, 2001). More activity reduction was observed with both Cr-MOR catalysts as most of the available active sites for VOC combustion were the one that lined the bigger channel. The accumulation of coke caused the zeolite catalysts to loose significant portion of their surface area as summarized in Table 3. The extent of area loss varied depending on the type of zeolite support. The worst was observed with both Cr-MOR catalysts, explaining more deactivation as observed in Figure 4(a). Meanwhile, Cr-ZSM-5 catalysts were the ones that least affected by coking and the stability improved with higher Si/Al ratio support.

Data in Table 3 show that upon treatment with ethyl acetate at 400°C for 48 h, Cr-MOR(40) experienced more drop in S_{BET} compared to Cr-MOR(90). However, it was Cr-MOR(90) that suffered more reduction in activity as suggested by Figure 4(a). This contradiction could be explained based on several reasons. It was expected that at lower Si/Al ratio, Cr-MOR(40) was less hydrothermally stable and might have experienced significant framework loss after 48 h and the effect was observed as heavy S_{BET} loss. However, chromium atoms in this catalyst, which was higher in amount compared to Cr-MOR(90) might still be available for ethyl acetate combustion. It was also possible that the main combustion reaction and coke formation occurred on different sites. In this circumstance, loss of surface area due to coke accumulation did not necessarily lead to corresponding loss

Table 3. Effect of Catalyst Deactivation on Their Surface Characteristics.

Catalyst	Percent effect on*		
	S_{BET}	Micropore area	Mesopore area
Cr-BEA(25)	-79.9	-92.8	-50.6
Cr-BEA(50)	-20.0	-19.7	-41.4
Cr-MOR(40)	-90.0	-97.2	-54.3
Cr-MOR(90)	-21.9	-19.4	-47.6
Cr-ZSM-5(90)	-60.8	-80.6	-38.0
Cr-ZSM-5(240)	-18.9	-12.2	-26.7

*Relative to fresh catalyst

of activity as the active sites (metal sites) on the catalyst were still available and accessible for reaction.

Coke analysis

Figure 5 depicts profiles of weight loss with temperature while the coked catalysts were heated in 20 ml/min of pure oxygen. For the purpose of clarity, only curves for Cr-BEA(50), Cr-MOR(90) and Cr-ZSM-5(240) were plotted as the effect of different Si/Al ratio on the characteristic weight loss was not clearly observed. Oxidation of coke initiated from 150°C with steady decrease in weight until a sudden drop detected in the 350°C to 550°C region depending on the types of sample. The temperature at which this drop occurred reflected the ease or difficulty for the coke to be oxidized. In the present study, the coke oxidizabilities were in the following order;

Cr-ZSM-5(240) > Cr-MOR(90) > Cr-BEA(50)

TGA results concluded that despite less prone to coking, Cr-ZSM-5(240) accumulated coke that was more stable to oxidation. In other words, it was more carbonaceous than that forming on Cr-BEA(50) and Cr-MOR(90) as confirmed by data in Table 4. This type of coke normally derived from molecules that were too large to enter the pores of this zeolite but only accumulated at the pore intersections. Through hydrogen transfer and dealkylation reactions, these molecules continued to become more carbonaceous and the effect was observed as lower overall H/C ratio. Softer and less carbonaceous cokes that accumulated on Cr-BEA(50) and Cr-MOR(90) normally formed by oligomerization or alkylation reactions within the zeolites (Chen et al., 1994).

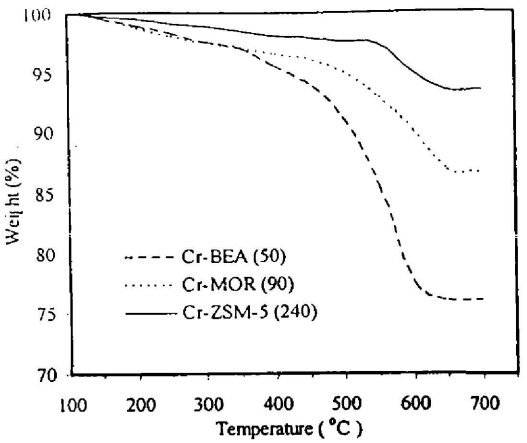

Figure 5. Profile of Weight Loss During Thermal Gravimetric Analysis for Three Different Chromium Exchanged Zeolites. (Conditions : 10°C/min, 20 ml/min Oxygen)

It is observed I Table 4 that zeolite beta-based catalysts were more prone to coking than mordenite-based catalysts but they experienced less deactivation as suggested by Figure 4(a). For example, Cr-BEA(50) accumulated 23.6 wt. % coke after 48 h but the ethyl acetate conversion dropped only to about 61 % while Cr-MOR(90) showed about 32 % conversion upon accumulation of 13.2 wt. % coke. This contradiction was due to several reasons. Despite experiencing almost similar

Table 4. Coke Content of the Used Catalysts and Their Corresponding H/C Ratio.

Catalyst	Coke content (wt. %)	Coke H/C ratio
Cr-BEA(25)	25.7	1.72
Cr-BEA(50)	23.6	1.56
Cr-MOR(40)	16.4	1.43
Cr-MOR(90)	13.2	1.28
Cr-ZSM-5(90)	8.6	0.88
Cr-ZSM-5(240)	6.4	0.72

treatment with ethyl acetate for 48 h, the actual S_{BET} of coked Cr-BEA(50) was still higher (332 m^2/g compared

to 292 m^2/g for Cr-MOR(90)). Also the pore system of beta zeolite was larger than that of mordenite to lessen the effects of diffusion limitation posted by coke deposition. This was especially true if the coke forms on larger straight 12-membered ring channels of zeolite beta. The contradiction also led to the possibility that coke deposition to occur on different sites with sites that were actively involved in the combustion reactions.

CONCLUSIONS

Oxygenated VOCs were found to be both very reactive and produced high carbon dioxide yield. Aromatics were more stable due to resonance effect but the reactivity increased when the electron cloud in the benzene ring was perturbed by electron donor groups such as methyl group. Cr-ZSM-5(240) demonstrated the highest hydrothermal stability due to its high Si/Al ratio. Despite giving higher initial activity due to high metal loading, Cr-BEA(25) was less stable and deactivated rapidly, especially after 30 h time on stream but it showed the best carbon dioxide yield in the long run. The high coke formation in mordenite and beta zeolites was associated with their high acidity, the presence of interconnecting channels of different sizes and the relatively larger pore sizes compared to ZSM-5. The low coking tendency of both Cr-ZSM-5 catalysts was attributed to lower acidity and smaller interconnected pore system of uniform sizes. Coke forming on Cr-ZSM-5(240) was more carbonaceous and oxidized at higher temperatures.

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